KU LEUVEN

eu Rare
57-71
sustainable exploitation

Applying ionic liquids in the pre-processing of rare earths concentrates

EXIL

April 2016, Poznań

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  - ILs as organic solvents (undiluted-pure IL)
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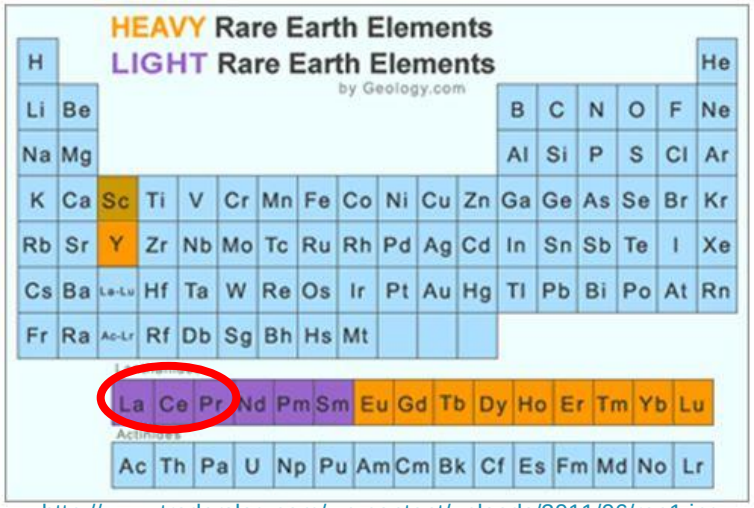
INTRODUCTION

57-71 eu Rare sustainable exploitation

- Rare earth elements (REE)
  - Magnetic, optical, spectroscopic … properties
  - Critical metals (EU)

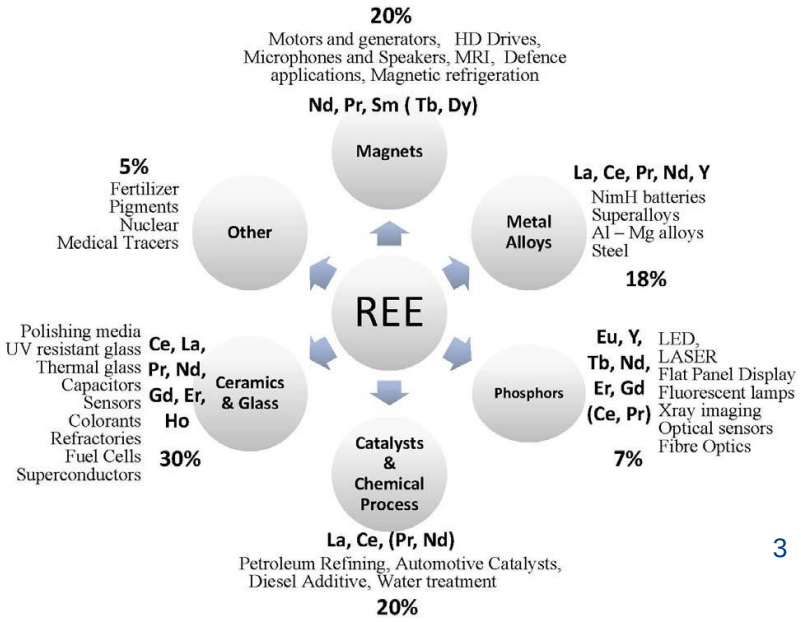


http://www.traderslog.com/wp-content/uploads/2011/06/ree1.jpg

- Increasing demand

1 kg of Nd, Pr, Dy for 1 hybrid car

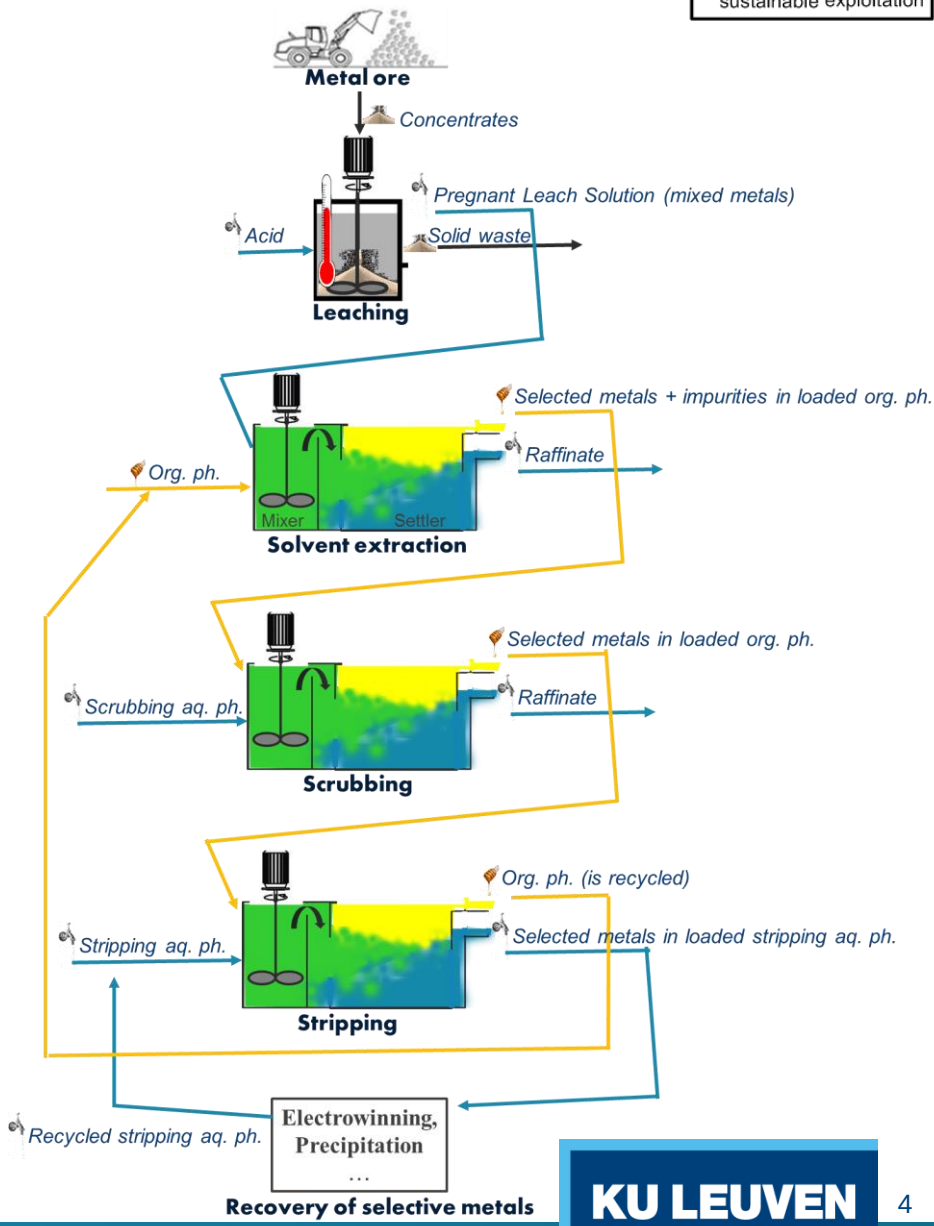
2.4 g of REE for one laptop computer



Percentage of the average world demand in 2006-2008

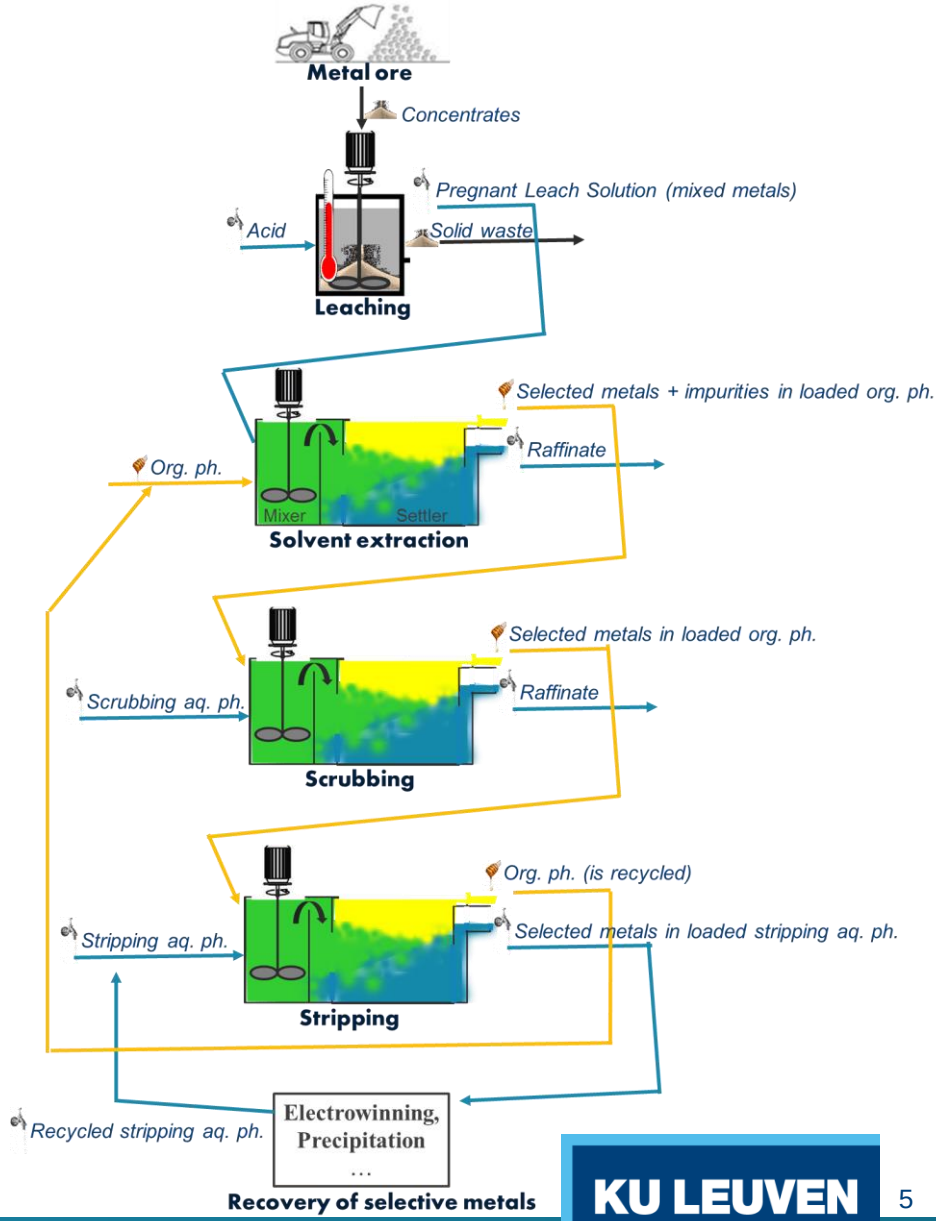
Solvent extraction, SX

- Ore mining and enrichment of the valuable minerals → *concentrates*
- Leaching to dissolve REE → *Pregnant leach solution* (PLS)
- Forcibly stirred with an immiscible organic solvent → *Loaded organic phase* *
- Disengagement of the two phases
- The different elements distributes differently
- Scrubbing aqueous solution *
- Stripping aqueous solution * (reverse)
  - Aq. phase: metal recovery (electrowinning, precipitation)
  - Org. phase: for recycling

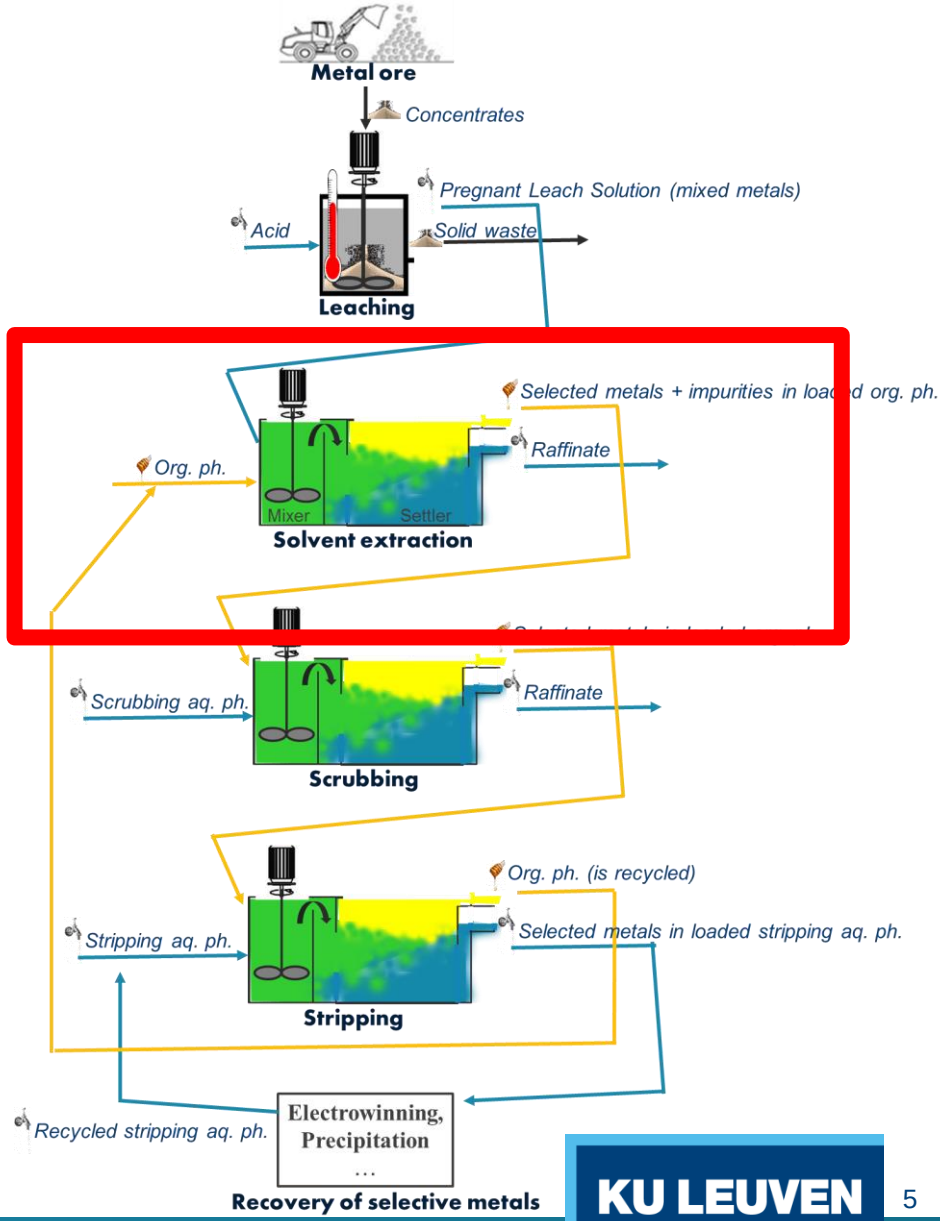


*Several stages

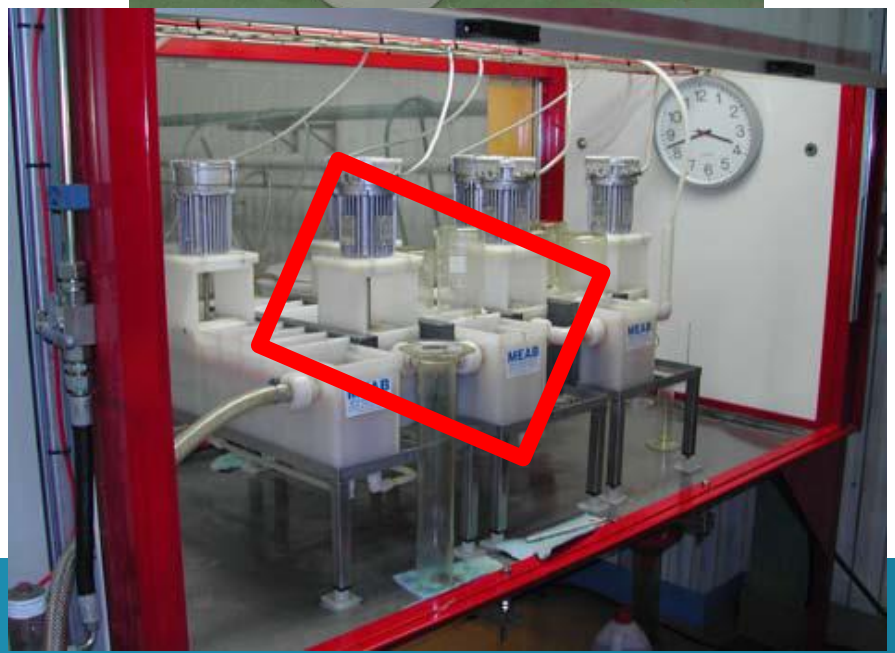
Pilot scale mixer-settler units

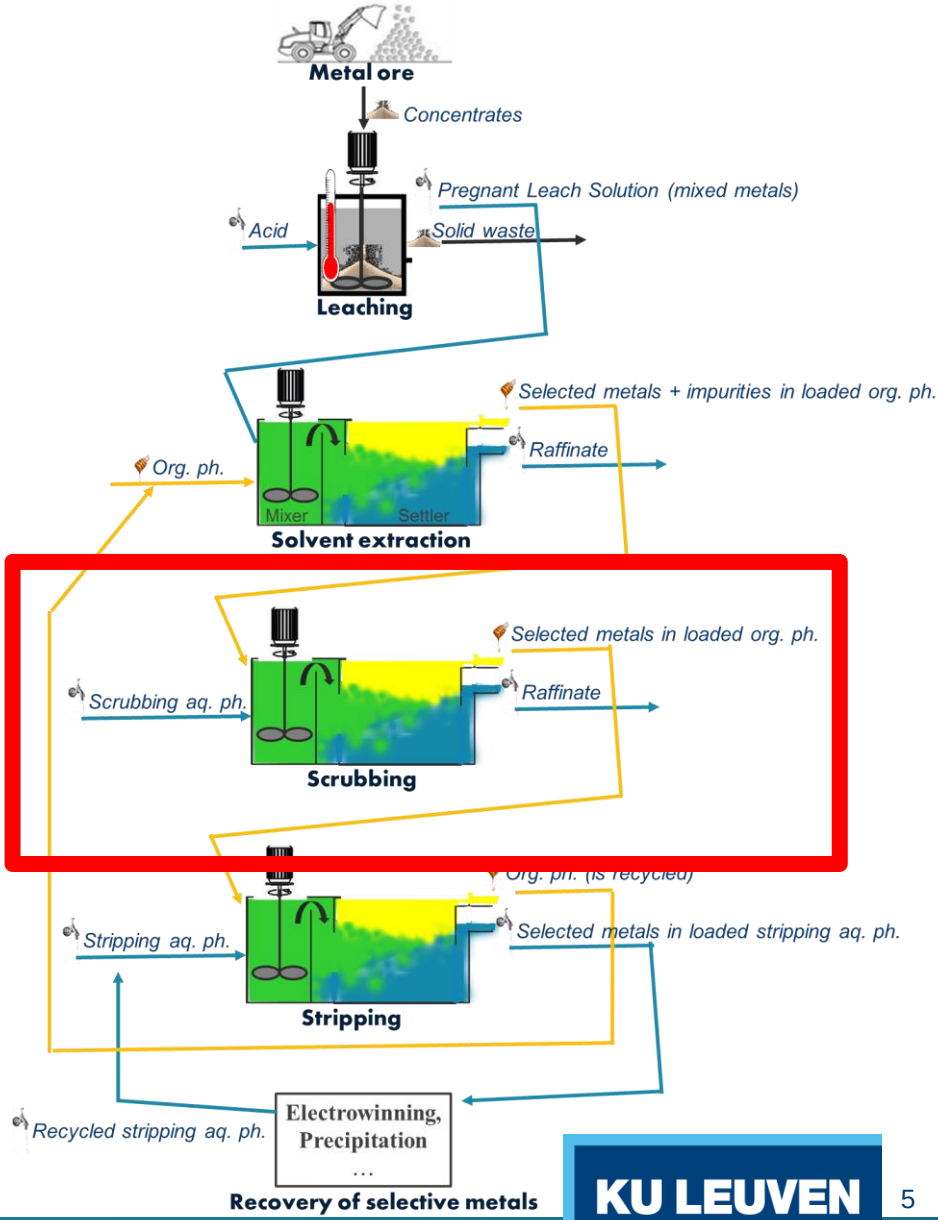


Pilot scale mixer-settler units

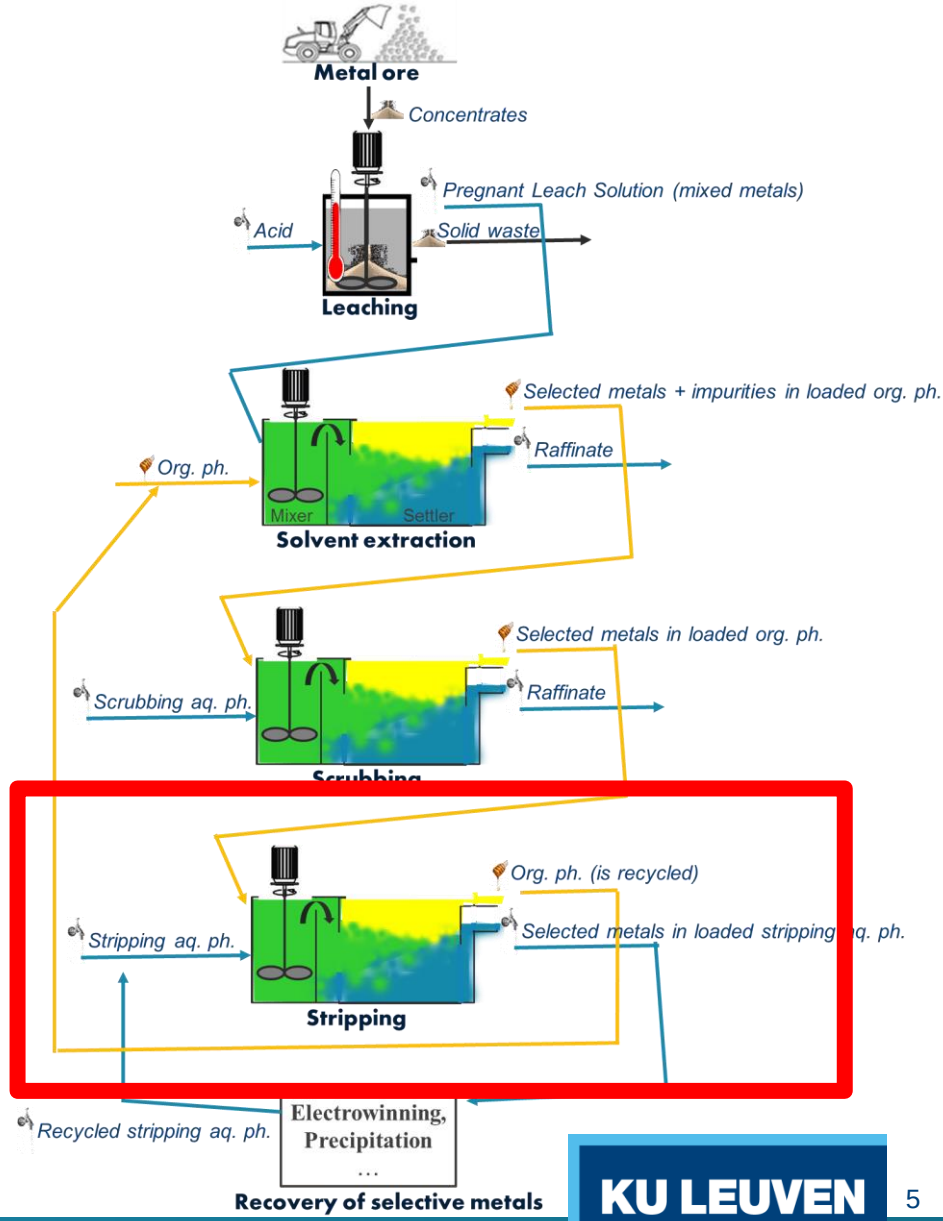


Pilot scale mixer-settler units





Pilot scale mixer-settler units



Sustainability

Safety Data Sheet
Kerosene

NFPA:

TESORO

SECTION 1. PRODUCT AND COMPANY IDENTIFICATION

Product name	Kerosene
Synonyms	Dual Purpose, K1, Dyed K1, Kerosene, Low Aromatic Feedstock, SPK Solvent, Arctic Grade Fuel Oil (DFA), Heater Oil, Range Oil, Coal Oil, K2, Gas Oil, 8881000048611
SDS Number	8881000048611 Version 2.16
Product Use Description	Fuel
Company	For: Tesoro Refining & Marketing Co. 19100 Ridgewood Parkway, San Antonio, TX 78259
Tesoro Call Center	(877) 783-7676 Chemtrec (Emergency Contact) (800) 424-9300

SECTION 2. HAZARDS IDENTIFICATION

Classifications	Flammable Liquid – Category 3 Aspiration Hazard – Category 1 Skin Irritation – Category 2 Specific Target Organ Toxicity (Single Exposure) – Category 3 Chronic Aquatic Toxicity – Category 2
Pictograms	
Signal Word	Danger
Hazard Statements	Flammable liquid and vapor. May be fatal if swallowed and enters airways – do not siphon by mouth. Causes skin irritation. Repeated or prolonged skin contact can cause skin irritation and dermatitis. May cause drowsiness or dizziness by inhalation. May cause irritation of respiratory system. Toxic to aquatic life with long lasting effects.
Precautionary statements:	
Prevention	Keep away from heat, sparks, open flames, welding and hot surfaces.

Safety Data Sheets (SDS)

SECTION 1-IDENTIFICATION

Product name: Toluene

Other names:-

Proper shipping name: Toluene

Recommended use of the chemical and restrictions on use:
The major use of toluene is as a mixture added to gasoline to improve octane ratings. Used as a solvent for paint, resins, lacquers inks & adhesives. Component of solvent blends and thinners. Used in the manufacture of chemicals, dyes, explosives, benzoic acid. Some grades of toluene may contain traces of xylene and benzene.
The use of a quantity of material in an unventilated or confined space may result in increased exposure and an irritating atmosphere developing. Before starting consider control of exposure by mechanical ventilation.
WARNING: Intentional misuse by concentrating/inhaling contents may be lethal.

Manufacturer/Supplier Name: Taiwan SM Corp., Kaohsiung plant
Address: NO.7, Industrial 1st Rd, Lin-Yuan Kaohsiung County 83203, Taiwan, R.O.C.
Phone No.: 886-7-6414511

Emergency phone No./Fax No.: 886-7-6414511 Ext. 221 (on duty), 886-7-6414517 (off duty)/886-7-6423828

SECTION 2-HAZARDS IDENTIFICATION

GHS Classification:
Flammable Liquid Category 2
Acute Toxicity (Oral) Category 4
Skin Corrosion/ Irritation Category 2
Serious Eye Damage/ Eye Irritation Category 2
Specific Target Organ Toxicity Repeated Exposure Category 2
Hazardous To The Aquatic Environment (Acute) Category 3
Aspiration Hazard Category 1

GHS Label elements:

Hazard symbols

Signal word
Danger

Hazard statements
Highly flammable liquid and vapor
Harmful if inhaled
Causes skin irritation
Causes serious eye irritation
May cause damage to organs through prolonged or repeated exposure.
May cause long lasting harmful effects to aquatic life.
May be fatal if swallowed and enters airways.

Precautionary statements
Use only in well ventilated area.
Control of exposure by mechanical ventilation in an unventilated or confined space.
Avoid breathing vapors and contact with skin and eyes.
Wear breathing apparatus/protective gloves/face protection.
Store in well-ventilated place.
Disposal must be in accordance with applicable federal, state, or local regulations.

Other hazards: –

SECTION 3-COMPOSITION/INFORMATION ON INGREDIENTS

CAS No.	Chemical Name	wt% by weight	EINECS No.
00108-88-3	Toluene	97.0 min.	203-625-9
Synonyms	**Methylbenzol; Methylbenzene; Toluol; Phenylmethane**		

Fluorine-free ionic liquids:

- Low volatile
- Non flammable
- Electrically conductive: static electricity is not accumulated

Objective

- ILs in SX to selectively separate lanthanum and cerium (La, Ce) from praseodymium (Pr).

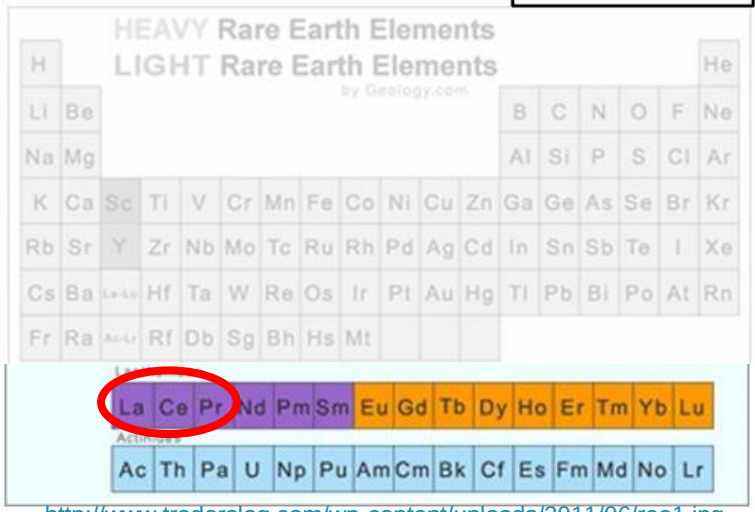
- ***Preprocessing:***

La(III),Ce(III) lowest economic value

La → NiMH, optical glasses and additive to alumina

CeO_2 → catalysts

- Consecutive REE are the most difficult to separate within the group, specially in chloride routes.



http://www.traderslog.com/wp-content/uploads/2011/06/ree1.jpg

GME RESOURCES LIMITED

TASMAN METALS LTD

TASMET AB(TASMET)

Johnson Matthey

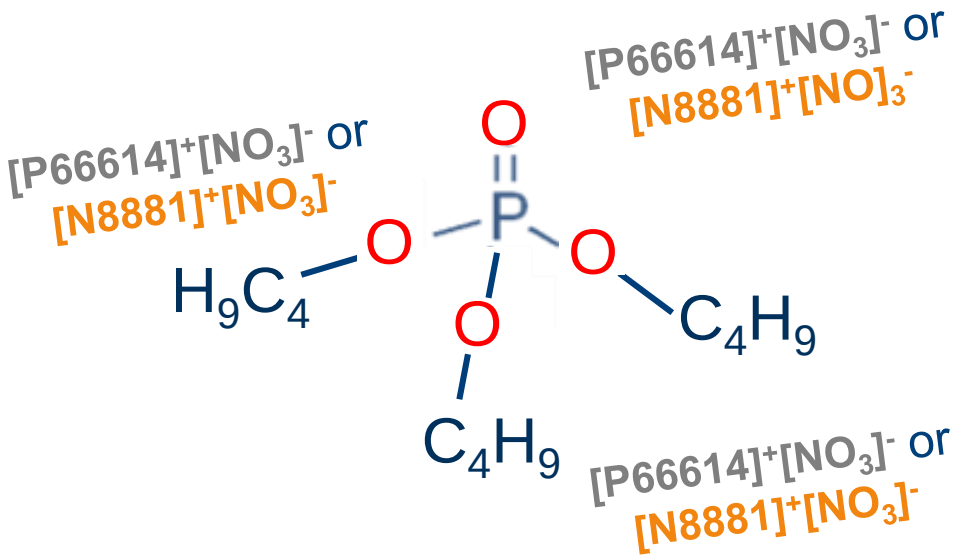
Johnson Matthey PLC (JM)

BASF We create chemistry

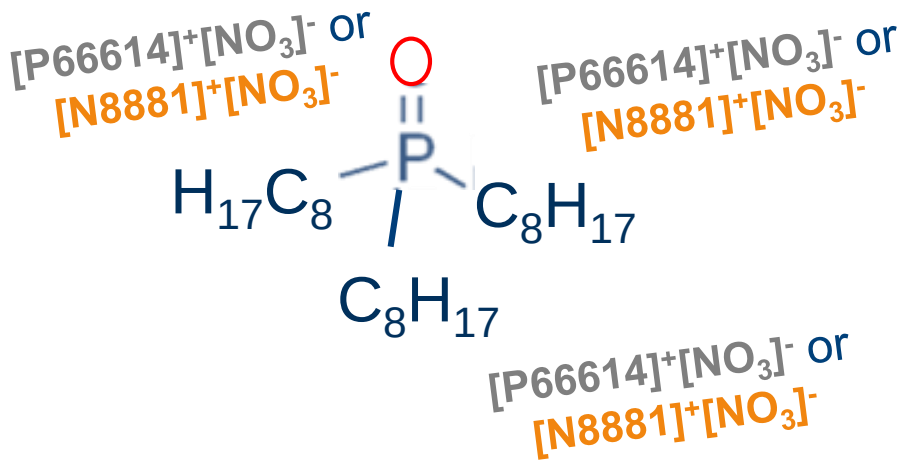
Materials (1): Organic phase

1. Pure ILs: **Cyphos101NO3**;$_{[P66614]^+[NO_3]^-}$ **A336NO3**:$_{[N8881]^+[NO_3]^-}$
   - A336: REEs extractant earlier than it was known as an IL.
   - A336 as pure IL (solvent) or as diluent, NOT diluted in molecular diluents

2. ILs as diluents of neutral extractants: TBP, Cyanex® 923



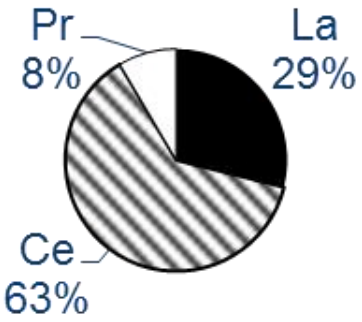
TBP



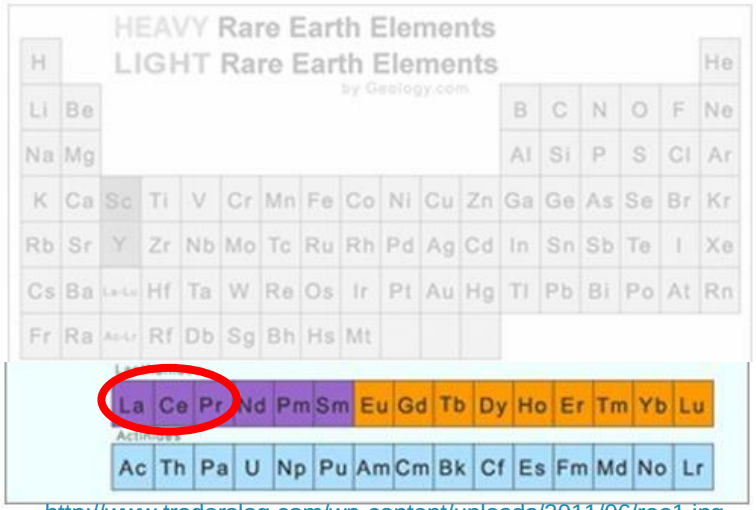
Cyanex® 923
(main compound)

Materials (2): Aqueous phase

HCl leaching of REE intermediate concentrate (carbonates, oxalates) based on the Norra Kärr ore (mineral Eudialyte)

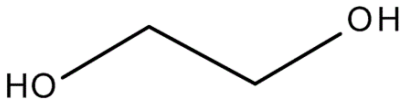


Norra Kärr, TREE 7-40 g/L (0.05-0.3 M)



http://www.traderslog.com/wp-content/uploads/2011/06/ree1.jpg

- Ethylene glycol (EG): polar organic solvent to decrease the H_2O surrounding the REE ions



Method: SX via Split-anion

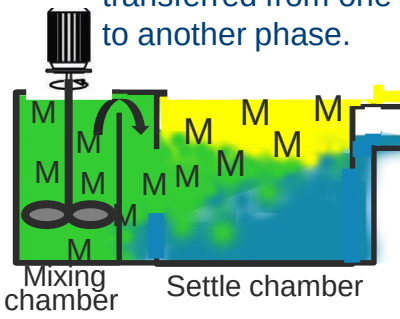
- Organic phase, IL (lighter-upper): anions for complexing and extracting the REEs (NO_3^-) (solvating extraction, no anion exchange)

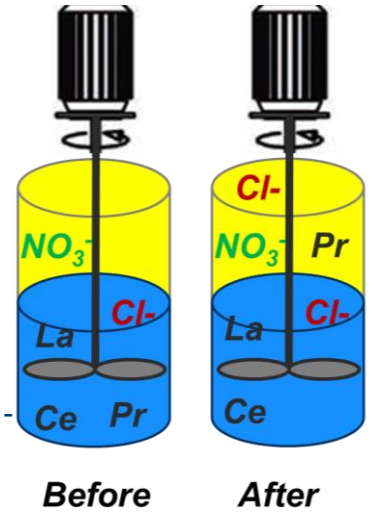
- Aqueous phase, feed solution (heavier-lower): other anions (Cl^-) that:
  - ✓ form weakly complexes with REE
  - ✓ stronger affinity to stay in the aqueous phase

- Order of preference for water: Hofmeister series

$SO_4^{2-} > HPO_4^{2-} > CH_3COO^- > Cl^- > Br^- > ClO_3^- > I^- > NO_3^- > ClO_4^- > SCN^-$

Selected element is transferred from one to another phase.





Mixed until equilibration in TMS-200 turbo thermoshaker, followed by centrifuging (3500 rpm, 5 min) to phase disengagement

K Larsson, K Binnemans. *Separation of rare earths by split-anion extraction* - Hydrometallurgy, 2015

DATA PROCESSING

Display the extraction data of an element compared to other elements

- Distribution ratio (D)
- Extraction porcentage (E)
- Separation factors ($\alpha_{A,B}$, $\alpha_{A,B+C}$)

$$D_A = \frac{[A]_{IL}}{[A]_{aq}} = \frac{[A]_{0,aq} - [A]_{eq,aq}}{[A]_{eq,aq}} \times \frac{V_{aq}}{V_{IL}} = \frac{[A]_{0,aq} - [A]_{eq,aq}}{[A]_{eq,aq}}$$

If volume ratio a:o = 1

Metal distributions and kinetics
can be adjusted varing different parametres:

- IL
- Temperature
- Mixing speed
- [Cl^-]
- Initial REE concentrations
- pH
- Composition of the org. ph.
- Polar organic solvent (aq. ph.)

$$\%E_A = \frac{D_A}{D_A + \frac{V_{aq}}{V_{IL}}} \times 100 = \frac{[A]_{eq,IL} V_{IL}}{[A]_{eq,IL} V_{IL} + [A]_{eq,aq} V_{aq}} \times 100$$

If volume ratio a:o = 1 → $\%E_A = \frac{[A]_{0,aq} - [A]_{eq,aq}}{[A]_{0,aq}} \times 100$

$$\alpha_{A,B} = \frac{D_A}{D_B}$$

Solutes A and B are those that make α >1

If volume ratio a:o = 1 → $\alpha_{A,B} = \frac{[A]_{IL}/[A]_{aq}}{[B]_{IL}/[B]_{aq}}$

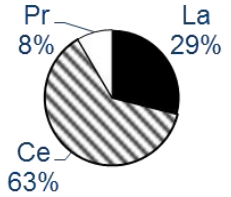
$$\alpha_{A,B+C} = \frac{D_A}{D_{B+C}} = \frac{[A]_{IL}/[A]_{aq}}{([B]+[C])_{IL}/([B]+[C])_{aq}}$$

If volume ratio a:o = 1

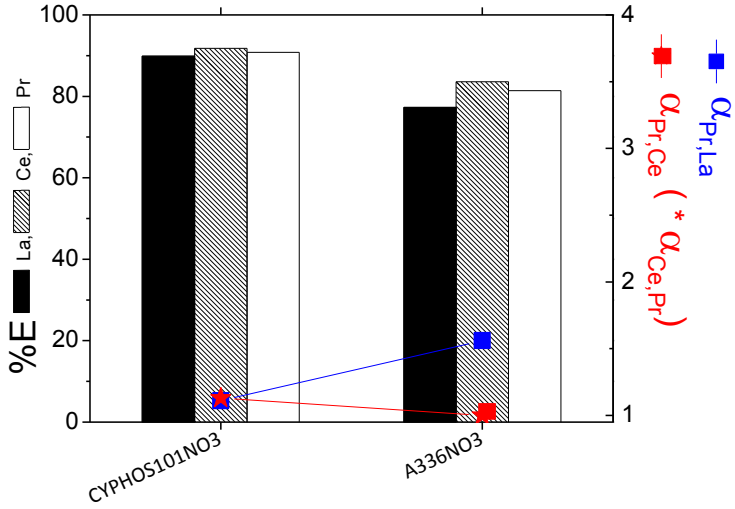
Rice, N. M., Irving, H., & Leonard, M. A. (1993). Nomenclature for Liquid-Liquid Distribution (Solvent-Extraction) (IUPAC recommendations 1993). *Pure and Applied Chemistry, 65*(11), 2373-2396.

Results: ILs

- IL
- Temperature
- Mixing speed
- [Cl-]
- Initial REE concentrations
- pH
- Composition of the org. ph.
- Polar organic solvent (aq. ph.)



Norra Kärr,
TREE 14 g/L (0.1 M)



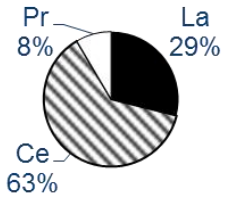
- Extraction of REE with both ILs is possible
- Reversed sequence: *%E* Ce > *%E* Pr
- A336NO3: lower extraction capacity, but higher $\alpha_{A,B}$ (more hygroscopic) A336NO3 formed emulsions

50ºC, 3000 rpm, 8 M Cl^-, initial pH: 0.08, final pH: 3-4, ratio 1:1v

Effect of T, rpm, [Cl^-], $pH_{initial}$

- Key parameters: mixing speed and chloride concentration
- Selectivity in the separation of La+Ce from Pr on intermediate *%E* (40-60%)
  - high excess of REE compared to the IL capacity to extract them

    enhance the competition between REE to form complexes and extract first the ones that show higher affinity to nitrates.



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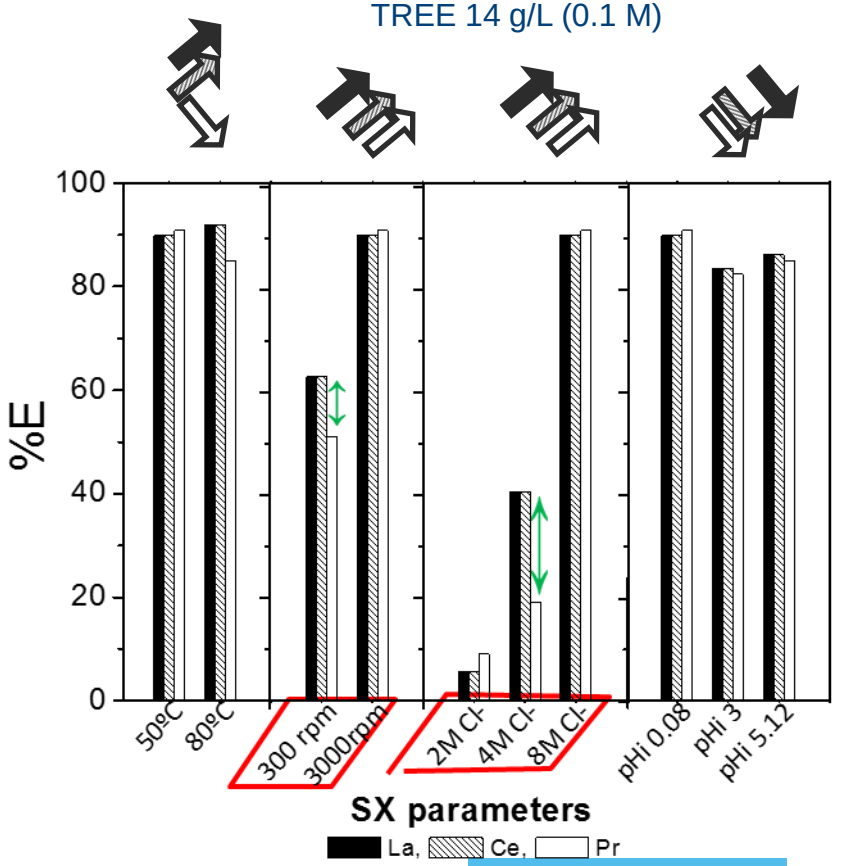
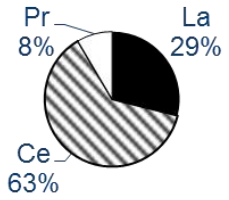


50ºC, 3000 rpm, 8 M Cl^-,pH ini: 0.08, pH eq: 3-4, ratio 1:1v, $[P_{6.6.6.14}]^+[NO_3]^-$

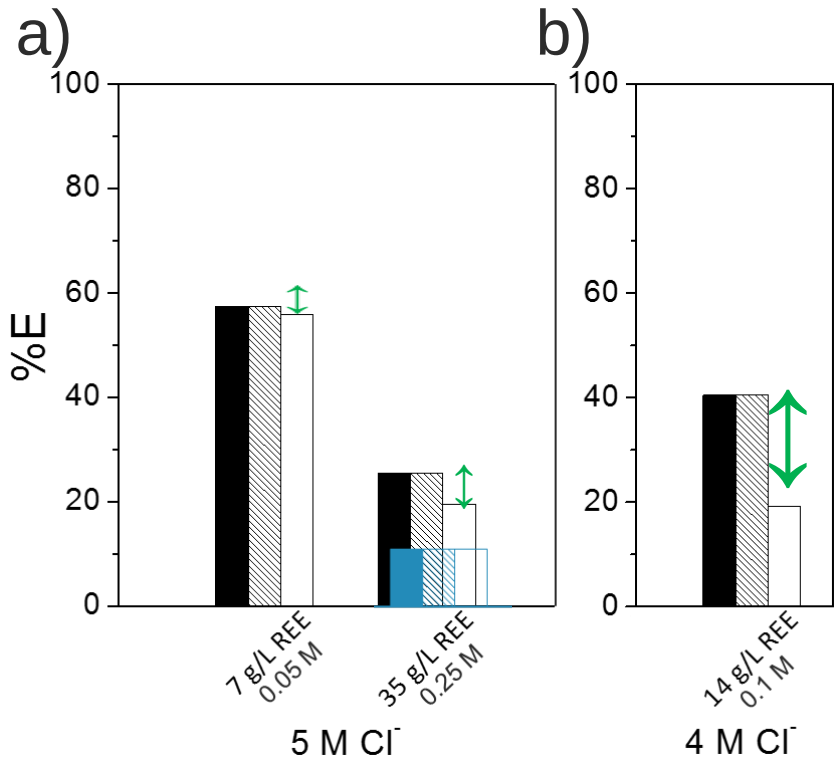
Effect of REE concentrations

÷ 2.6

- The decrease of *%E* is lower than that what would correspond
- Difficult to reach the **theoretical** maximum load capacity and, thus, high [REE]s in the aqueous phase are needed.
- Higher $\alpha_{La+Ce,Pr}$ if the overall extraction is hindered:
  - increasing the [REE]
  - decreasing the [chloride]



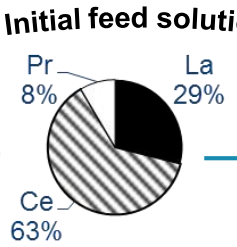
Norra Kärr,
TREE 7-35 g/L (0.05-0.25 M)



50ºC, 3000 rpm, initial pH: 0.08, final pH: 3-4, ratio 1:1v, Cyphos101NO_3

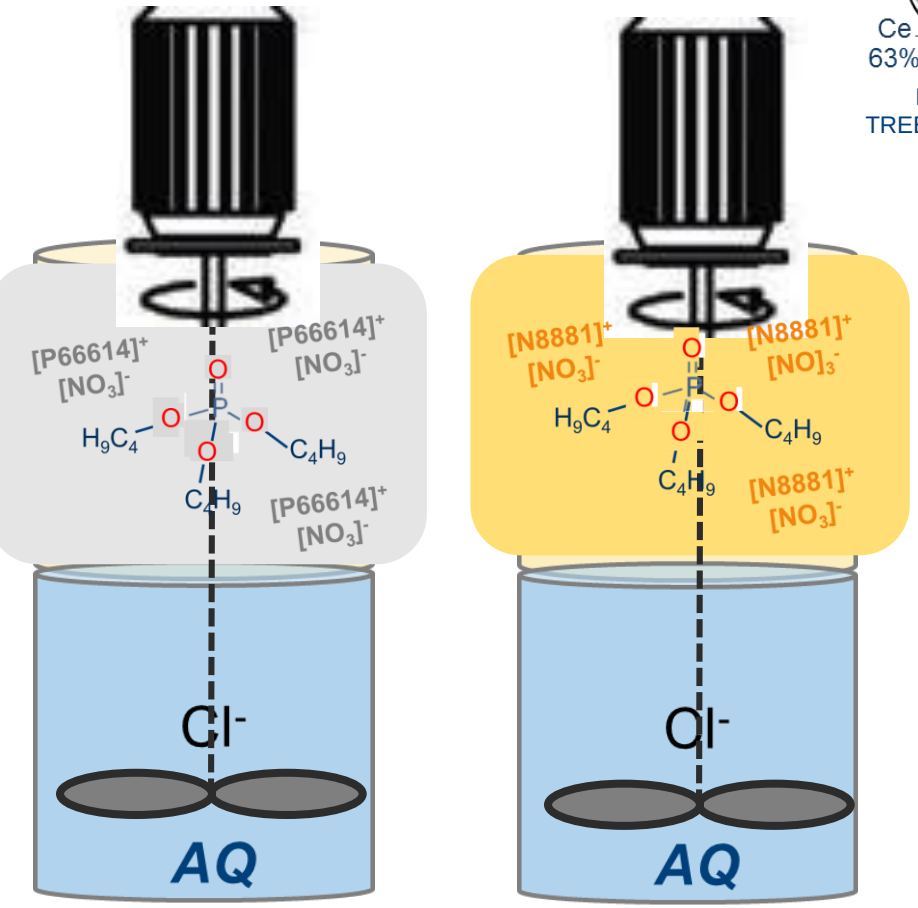
Effect of two neutral extractants in both ILs

Also similar for both ILs

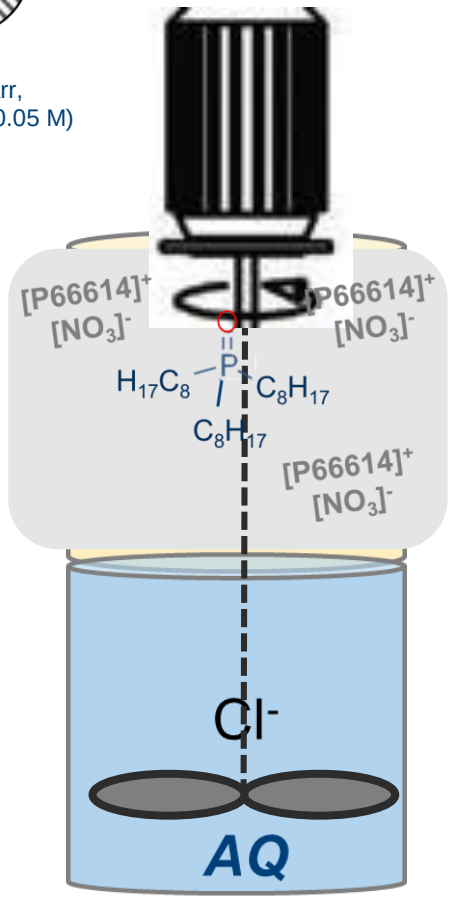


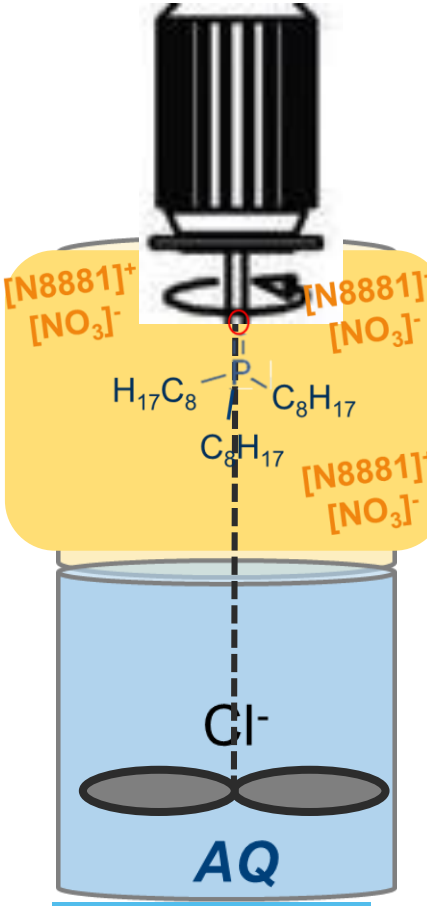
Norra Kärr,
TREE 7 g/L (0.05 M)

TBP (1-20 m%)



Cyanex® 923 (1-20 m%)





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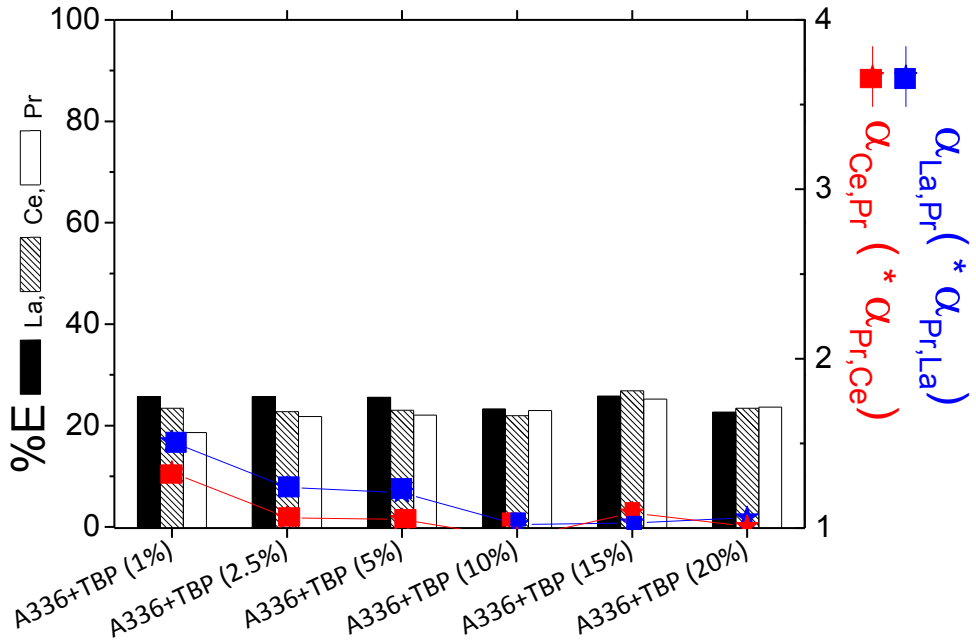
Difficulties in the phase separation of undiluted A336NO3 (even at low loading of REE and at high [salting-out agent]).
In contrast: easy phase disengagements with mixtures TBP/A336NO3 and Cyanex® 923 /A336NO3 in the organic phase.

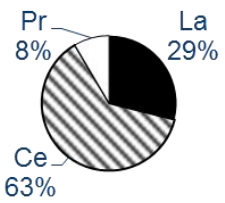
TBP

TBP no effect.

Low extraction values (D <0.4, *E* → 20-30%, $\alpha_{A,B}$→1.2)



Initial feed solution



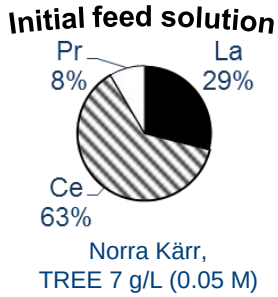
Norra Kärr,
TREE 7 g/L (0.05 M)

Only at 20 m% TBP, *%E* of Pr > *%E* of La, Ce

70-80ºC, 3000 rpm, 4 M Cl^-, initial pH feedsol: 5, initial pH Cyphos=1.85, initial pH A336: 2.80, final-EQ pH cyphos: 2.5, final-EQ pH A336: 3 ratio a:o 1:1v, 7 g/L REE

Cyanex® 923

- Increase of *%E*:
  - Phosphine oxides have high Gutmann donor number, resulting in stronger interactions with the Lewis acidic REE-nitrate complex
- Extraction sequence is reversed back to a positive order
  - %E of Pr > %E of Ce and La
  - Reduction of the organic phase and extraction stages needed
  - The separation factors follow a bell curve



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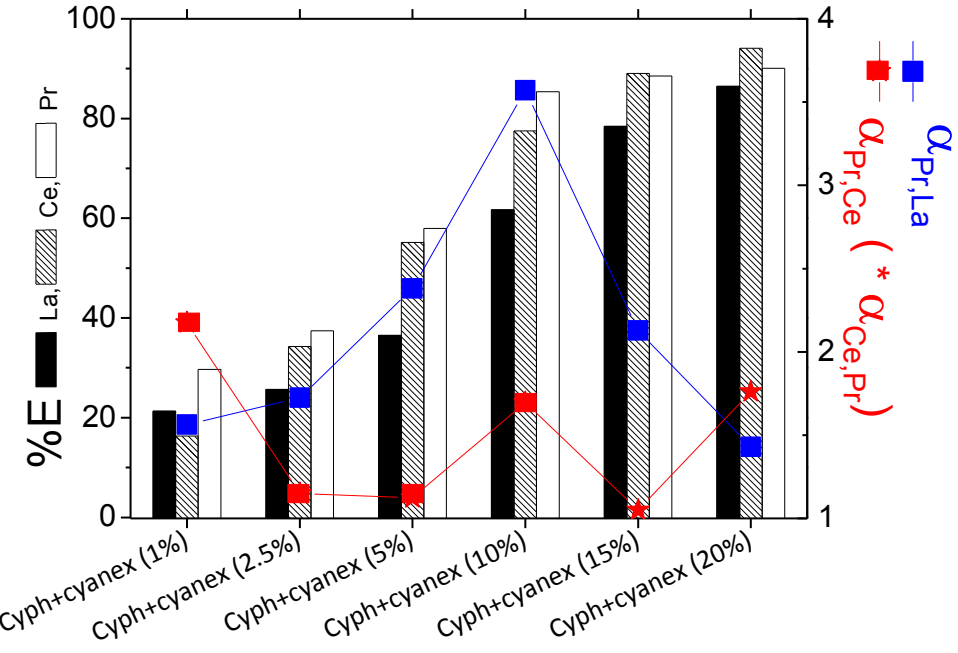
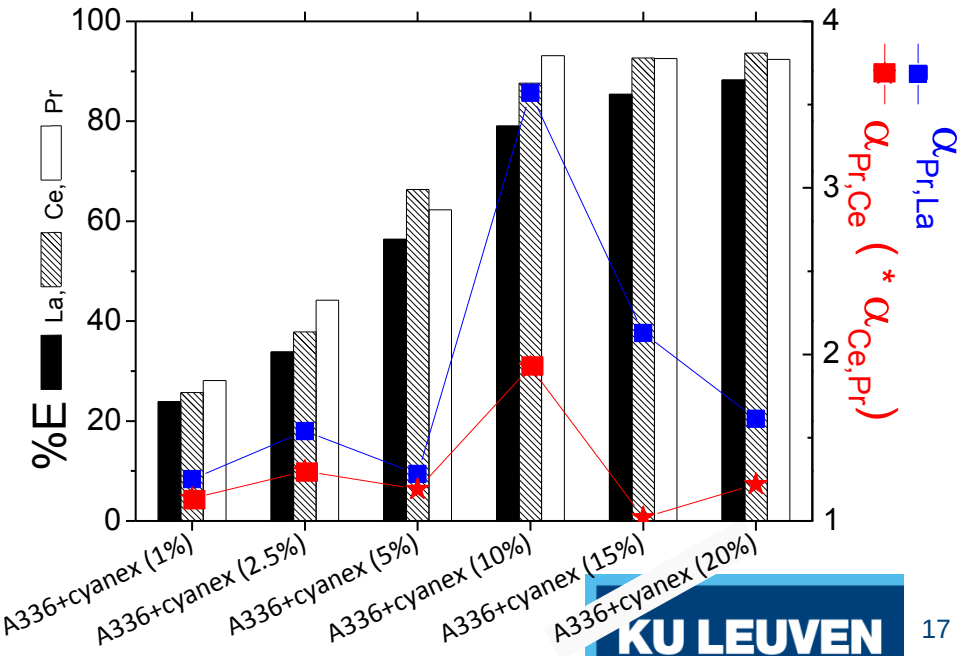
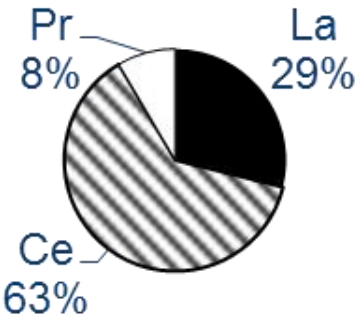


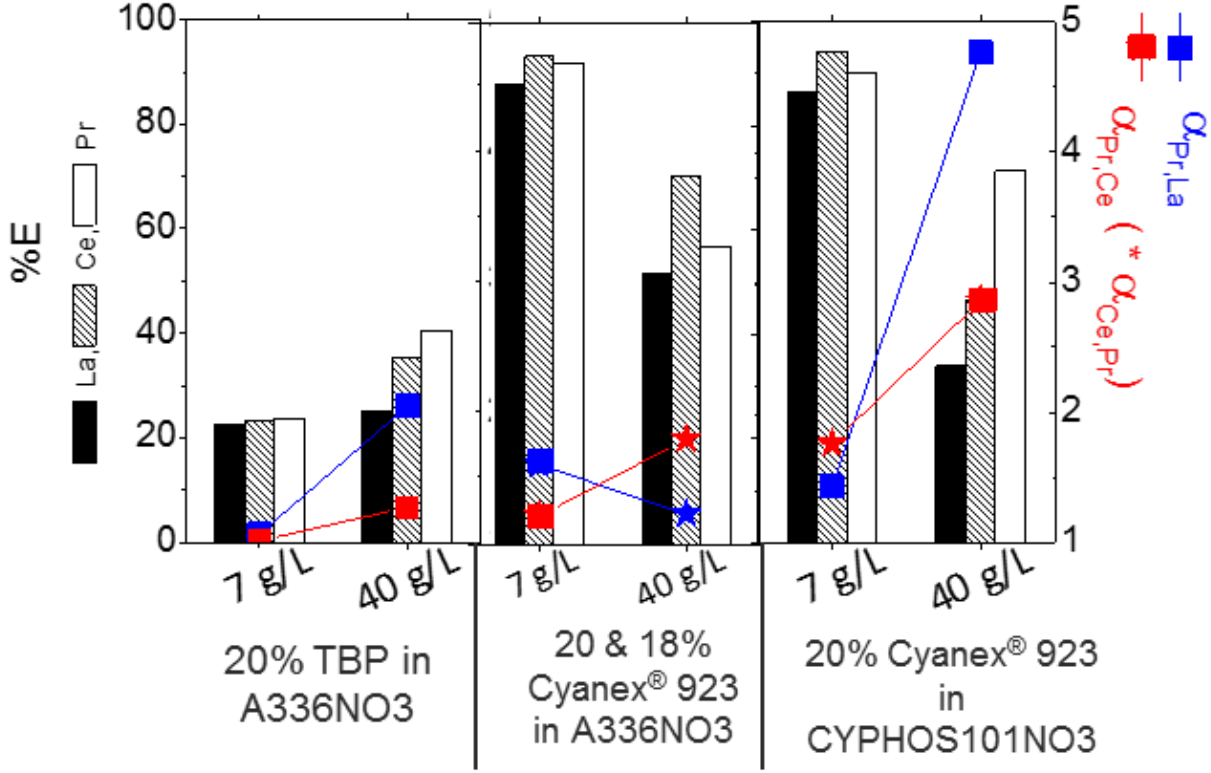


70-80ºC, 3000 rpm, 4 M Cl^-, initial pH feedsol: 5, initial pH Cyphos=1.85, initial pH A336: 2.80, final-EQ pH cyphos: 2.5, final-EQ pH A336: 3 ratio a:o 1:1v, 7 g/L REE

Effect of [REE] and organic phase composition

- Selectivity increases with the [TREE]
- With TBP/IL → less efficient system than Cyanex® 923





High affinity of Cyphos+20% Cyanex® 923, towards Pr at high [REE]

(generally, in chloride routes via solvation, the $\alpha_{La,Ce}$ 1.6)

70-80ºC, 3000 rpm, 4 M Cl^- , 20 v% extractant (0.52 M)

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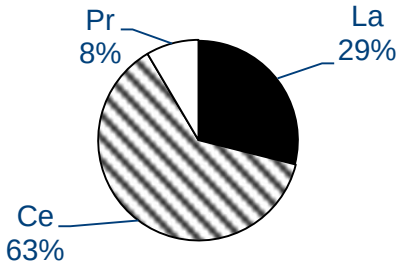
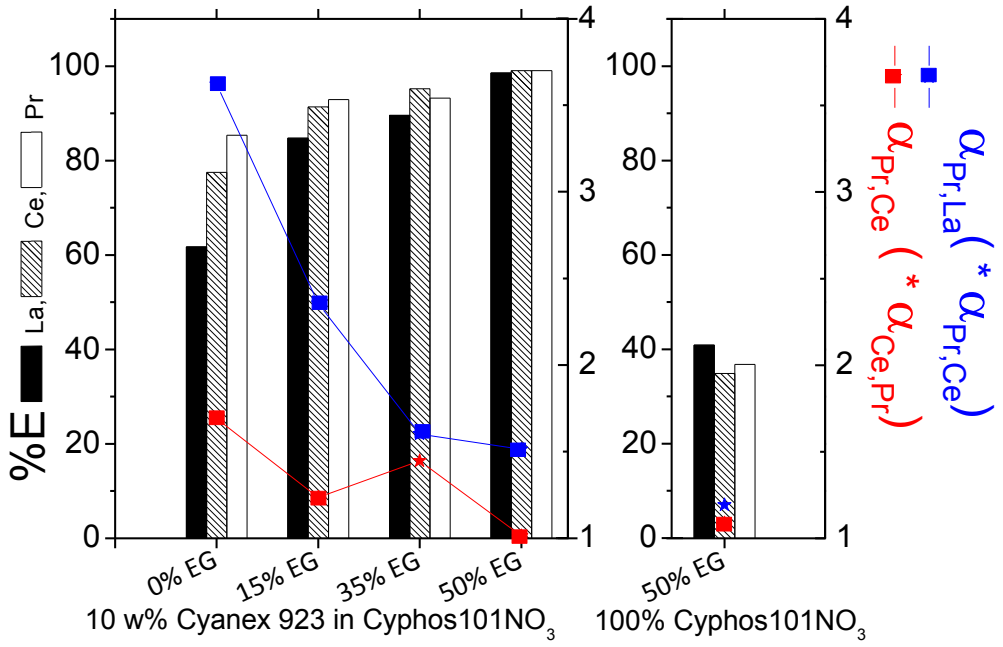
RESULTS: EG IN THE AQ. PH.



7 g/L TREE
10 wt% Cyanex 923



- Increment of the extraction, but its effect is irrelevant compared to the extractant dissolved
- Decrease of the separation factors

80ºC, 3000 rpm, 4 M Cl^-, pHeq cyphos: 2.5, ratio aq:IL 1:1v, 10 wt% Cyanex 923

CONCLUSIONS

~~A336NO3~~ ~~TBP~~ ~~EG~~

- Cyphos101NO_3 with 20% Cyanex® 923 (org. ph.) and 5 M Cl^- (aq. ph.) to separate Pr from La and Ce.
  40 g/L TREE: 70% E Pr, vs. 34% E Ce, La
- Possibility of using neutral extractants in SX from chloride solutions.
- Cyanex® 923 diluted in both ILs is a synergistic agent for SX.
- At higher [REE], better selectivity in Cyphos101NO_3.
  Competition to form complexes that can be extracted from the aq. to the org. phase.

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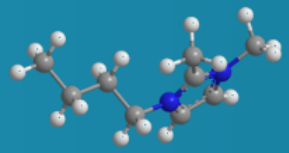

EXIL

cost EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

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- All of you for your attention

SEVENTH FRAMEWORK PROGRAMME

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